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ANALYTICAL CHEMISTRY NEEDS FOR NUCLEAR SAFEGUARDS IN NUCLEAR FUEL REPROCESSING

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ABSTRACT

A fuel reprocessing plant designed to process 1500 tonnes of light water reactor fuel per year will recover 15 tons of Pu during that time, or approximately 40 to 50 kg of Pu per day. Conventional nuclear safeguards accountability has relied on batch accounting at the head and tail ends of the reprocessing plant with semi-annual plant cleanout to determine in-process holdup. An alternative proposed safeguards system relies on dynamic material accounting whereby in-line NDA and conventional analytical techniques provide indications on a daily basis of SNM transfers into the system and information of Pu holdup within the system.[1] This paper will attempt to describe some of the analytical requirements and problems for dynamic materials accounting in a nuclear fuel reprocessing plant. Some suggestions for further development will be proposed.

INTRODUCTION

Conventional nuclear safeguards accountability in a nuclear fuel reprocessing plant is based on dividing the process into item control areas (ICA) and material balance areas (MBA). The areas are: (1) fuel receiving (ICA), (2) reprocessing (MBA), (3) wastes (ICA), (4) analytical chemistry (MBA), (5) plutonium loadout (MBA). In this paper we will concentrate on areas (2) and (3).

Figure 1 shows the material flow in a reprocessing plant from the dissolver through fission product separation and U-Pu partitioning. Figure 2 shows the material flow through the Pu purification section of the plant.

In the reprocessing area the conventional material balance is based on input measurements at the accountability tank and output measurements at the Pu product tank and in the waste streams. Each dissolver batch is sampled at the accountability tank and isotope dilution mass spectrometry is generally used to measure both Pu and U concentrations. Isotopic analysis also permits the correlation of the fuel element composition with reactor

engineering data. This is an important safeguard to ensure that a substitution has not been made by the shipper or in transit. Isotope dilution has been proven to be both precise and accurate for major isotopes and, for total Pu and U concentration, a RSD of 0.1 to 0.2% can be obtained. In practice, however, interlaboratory checks may differ by 0.5 to 1%.

System holdup is measured on a semiannual flushout-cleanout inventory. For a 1500 MT/year plant the holdup in the plutonium process area is approximately 50 kg of Pu, or equal to the average daily throughput.[2] Seven or eight tons of Pu pass through the system between holdup inventories.

The proposed safeguards system[1] relies on dynamic material accounting whereby in-line NDA techniques and conventional analytical methods can provide timely indications on a daily basis of special nuclear material transfers into the system and the Pu holdup within the system. To optimize the dynamic materials accounting procedure, the plant may be divided into several material balance areas. To simplify the analytical process, the concept of graded safeguards is introduced--that is, the maximum information is obtained and processed from the Pu purification area where the Pu is in the most concentrated pure form, hence the form most attractive for diversion.

Some of the areas where additional work on analytical methods might be required for improved safeguards accounting methods are shown in Table 1. The analytical methods selected must be rapid, as free as possible from interferences, and must be applicable to radioactive reprocessing solutions. The analyses may be performed in-line (the measurement is made directly in the process stream), on-line (the measurement is made in a by-pass line from the main stream but the material is returned to the process stream without chemical alteration), or at-line (a portion of the process material is withdrawn from the process stream).

RADIOLYTIC PROBLEMS

The high radiation fields encountered throughout the reprocessing area can result in potential problems for the analytical chemist.

The Purex process is based on the extraction of U and Pu from a HNO_3 solution with tributyl phosphate (TBP) dissolved in a hydrocarbon solvent. At radiation exposures exceeding several tenths Wh/L, TBP decomposes to dibutyl phosphate (DBP) and monobutyl phosphate (MBP), with a

TABLE 1. SOME AREAS FOR IMPROVED ANALYTICAL METHODS

Area	Method	Comments
Leached hulls	$^{144}Ce/Pu$	Assumes no partitioning of R.E.s and Pu in hulls.
Centrifuge sludge	Not measured	High β, Y; primarily Zr but can contain 0.1% of fissile material.
1BP line	Not measured	5 g/L Pu, 10 g/L U; some F.P's. Absorption edge densitometry; X-RF.
2AW, 3AW, 3PD	α monitor	Recycle aqueous wastes; require added evaluation.
2BW, 3BW	α monitor	Recycle organic wastes; require added evaluation.
3PCP	Not measured	Absorption edge densitometry ~250 g/L.

mole ratio of approximately 9:1 of DBP:MBP.[3,4] Both complexes are very stable and do not behave in the extraction process as do TBP complexes. The highest radiation exposure levels for the TBP are at the front end of the separations system (the HA contactor) where the initial separation of fission products from the U and Pu is performed. The extraction behavior of DBP and MBP complexes of U and Pu is a complex function of U and Pu concentrations, acid concentration, and DBP and MBP concentrations. At the 1BP column (2.6 M HNO_3) Pu complexes of DBP tend to dissolve in the organic phase and MBP complexes in the aqueous phase. At high U concentrations Pu is forced to the MBP complex and hence into the aqueous phase. This Pu is not extracted into the organic phase in the 2A column, but is routed to the acid wastes, requiring that Pu analytical methods be capable of determining both complex and labile Pu. For example, in the 1BP line and in the 2AW waste stream the analyst must be aware that Pu can be present not only as the nitrate but as a stable MBP complex.

At the product end of the process, high Pu concentrations result in radiolytic decomposition of the H_2O and HNO_3. The major reactions for H_2O decomposition result in the net conversion of the solvent to H_2O_2, H_2, and some O_2. The rate of the radiolytic decomposition of H_2O is decreased by increasing the acid concentration. For HNO_3, the decomposition products are HNO_2 and H_2O.

The radiolytic reactions have a significant effect on the Pu solution chemistry. The decrease in solvent content leads to a slow increase in Pu concentration. The H_2O_2 formed will reduce any Pu(VI) to Pu(IV) and oxidize Pu(III) to Pu(IV). During a two-week storage period in 8 M HNO_3 Pu is reduced almost quantitatively to the tetravalent state.[6] Disproportionation of Pu(IV) to form Pu(III) and Pu(VI) is not a problem at high acidities, but could become significant below 0.3 M HNO_3.[7]

An important consequence of radiolysis lies in the fact that most analytical methods for determining Pu were developed using weapons-grade Pu, which is predominantly ^{239}Pu. Commercial reactor-grade Pu contains significant concentrations of ^{238}Pu (an intense alpha emitter) and ^{241}Pu (an intense beta emitter). Because a higher probability exists for radiation-induced reactions, greater care must be exercised to minimize these reactions during analysis. Precision and accuracy for analysis of reprocessing solutions generally will be poorer than literature values obtained for weapons-grade material.

A method for determining U and Pu as the tetrapropylammonium complexes has been proposed[8] that might be applicable for determining both U and Pu in reprocessing-plant waste streams. In this method the tetrapropylammonium complexes are extracted into methyl-isobutyl ketone (MIBK) to effect a separation from fission products and other possible interfering elements. Simple ketones can undergo radiolytic decomposition to form alkenes, CO, and H_2,[9] and possibly the MIBK solvent could undergo such similar degradation. The carbon-nitrogen bond in primary, secondary, and tertiary amines is radiosensitive.[10] Quarternary amines in the form of choline and its analogs also are susceptible to radiolytic damage, yielding tertiary amines as the main product.[11,12] The radiation effects on the proposed separation have not been studied, but it is conceivable that separation characteristics involving long contact times and highly radioactive materials may be different from published data.

C. Polymerization

Polymerization has been recognized since the 1950s as a serious problem in the accountability of Purex process solutions.[13] Polymerization is a function of Pu and acid concentrations, and temperature and only occurs with Pu(IV). Polymer formation can result in loss of Pu through precipitation in storage tanks and adsorption on walls of pipes and tanks. Polymeric Pu is not included

in the results from some analytical schemes such as coulometric titrations. Plutonium nitrate should never be stored at acid concentrations <0.5 N, and a range of 2-10 N is recommended. Even a localized instantaneous decrease in acid concentration can cause polymerization; therefore, $Pu(NO_3)_4$ solutions should be diluted only with HNO_3, never with H_2O. Depolymerization can be hastened by an increase in temperature or acid concentration, or oxidation or reduction to Pu(VI) or Pu(III). The rate of depolymerization is dependent on the conditions under which the polymer was formed; high-temperature polymers are more stable and hence more difficult to depolymerize.[14]

FLOW AND CONCENTRATION MEASUREMENTS

One of the key factors in implementing a dynamic materials accounting system is the timely availability of information concerning movement of SNM in the process. The measurements must include data on concentration and on flow rate. Orifice meters in metering headpots, and ultrasonic or magnetic flow meters in pipes, with proper calibration, should be capable of providing flow data with accuracies and relative standard deviations of 1% or better without interfering with normal process operations.

Concentration can be measured by chemical or NDA means, with the latter preferred for timeliness. Some NDA methods that might be considered include:

Alpha Monitors: These are used in most reprocessing plants to measure Pu concentrations in waste streams, but have been designed basically for process control applications. With suitable calibration they may measure waste-stream concentrations with accuracies of 5 to 10%, which might be adequate for safeguards applications. They are isotope sensitive, and are particularly sensitive to ^{238}Pu. Hence, some knowledge of isotopic concentration in the streams is required.

Gamma-Ray Techniques: These can provide accuracy and precision of 1% or better, and systems have been designed for in-line measurements of both uranium and plutonium. The method is isotope sensitive, but ^{240}Pu and ^{242}Pu cannot be measured reliably.

Gamma-Ray Densitometry: Several prototype instruments have been developed and are being evaluated for safeguards applications. The method is not isotope sensitive. Precision and accuracy of better than 1% can be obtained in a measurement time of a few minutes. However, the

method is sensitive to all heavy and medium Z elements and does not appear suitable from a safeguards standpoint.

X-Ray Densitometry: An on-line x-ray absorption measurement of Pu in the Pu purification area of a fuel-reprocessing line using x-rays in the 25 to 50 keV region has been described.[15] The precision is approximately 2% for concentrations between 2 and 10 g/L. As with gamma-ray densitometry, the method is not isotope sensitive but is subject to serious interference by heavy elements.

Absorption-Edge Densitometry: This technique probably is the most versatile for safeguards measurements. It is element rather than isotope sensitive, and is capable of providing precision and accuracy of 1% or better with measurement times of a few minutes. Either K or L-III edges can be used, and energies can be selected so that the measurement is sensitive only to the element of interest. The technique has a further advantage over other NDA procedures under conditions typical of coprocessing or in the Th fuel cycle where U and Pu, or U and Th could be measured simultaneously. The method is being extensively investigated at Los Alamos for on-line measurements.

SUMMARY

Much of Pu analytical technology is applicable to nuclear fuel-reprocessing plants. However, methods should be evaluated to establish precisions for Pu measurements using the isotopic composition expected in a reprocessing plant.

Conventional electrometric methods for measuring Pu, having a relative standard deviation of 0.2% or better, will be required for evaluation of NDA on-line methods, and for daily calibration checks of NDA instruments. The automated spectrometric method for determining U and Pu in waste streams can be used for calibration of in-line alpha monitors, or to replace the alpha monitors, but should be evaluated further with regard to its usefulness in high-radiation environments.

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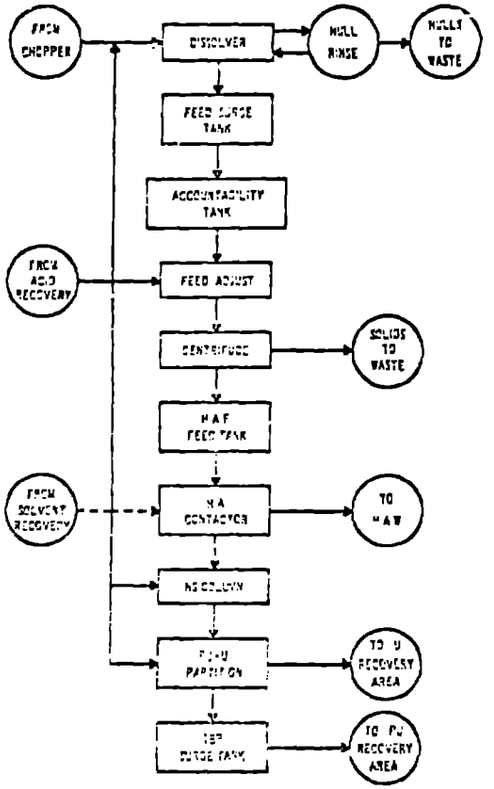

Figure 1. Dissolver-separations process block diagram.

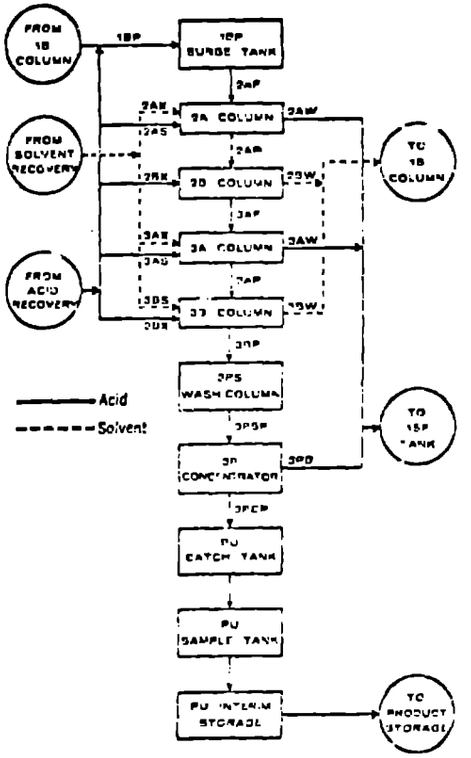

Figure 2. Plutonium purification process block diagram.